A STUDY OF THE KINETICS OF THE IODINATION OF DEUTERATED ACETONE CATALYZED BY ACIDS AND BASES

by

JOHN IGNATIUS GENEROSA

B. Sc.

1959

THE UNIVERSITY OF ALBERTA

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A DISSERTATION
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR
THE DEGREE OF MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

by

JOHN IGNATIUS GENEROSA
B. Sc.

September 15, 1959

UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES

The undersigned hereby certify that they have read and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "A Study of the Kinetics of the Iodination of Deuterated Acetone Catalyzed by Acids and Bases", submitted by John Ignatius Generosa, B. Sc., in partial fulfilment of the requirements for the degree of Master of Science.

ABSTRACT

A STUDY OF THE KINETICS OF THE IODINATION OF DEUTERATED ACETONE CATALYZED BY ACIDS AND BASES

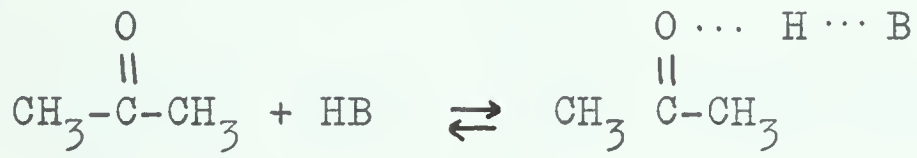
The kinetics of the reaction between iodine and deuterated (d_6) acetone in aqueous media catalyzed by acids and bases were followed spectrophotometrically at 460 mμ wavelength. The aqueous media consisted of the following weak acid and base pairs: acetic acid - acetate ion, monochloroacetic acid - monochloroacetate ion, glycollic acid - glycollate ion, and trimethylacetic acid - trimethylacetate ion. The catalytic constants (k) were evaluated for these species as well as for the oxonium ion. All reactions were carried out in sealed tubes at 25 ± .05°C and at a constant ionic strength of .150. The progress of each reaction was followed by recording the disappearance of iodine.

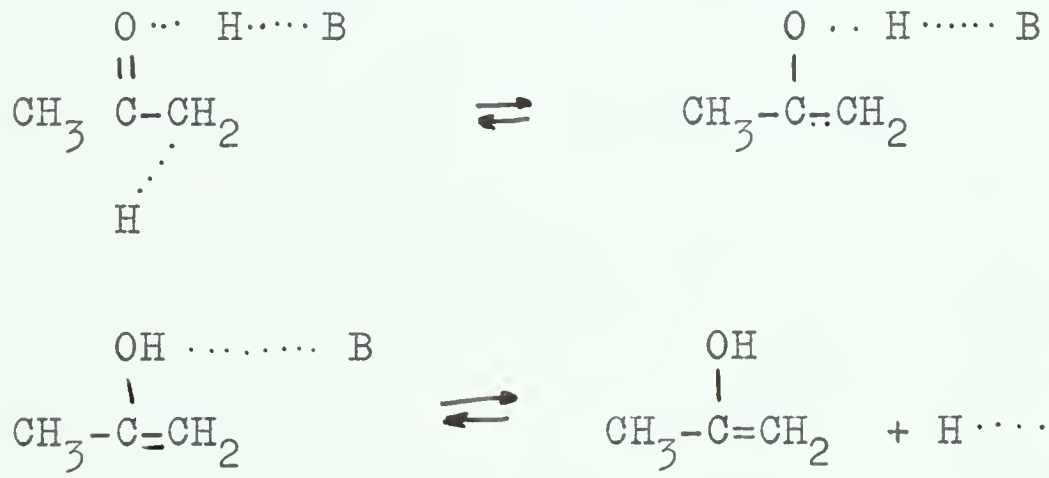
In all cases the reaction was zero-order with respect to iodine, first-order with respect to the undissociated acid, first-order with respect to the corresponding anion and first-order with respect to the oxonium ion. Because of the low concentrations of weak acid and base used (maximum concentration .150 M), a term of the form k_T [ACID] [ANION], although probably present, could not be shown to be definitely so, as its effect would be masked by experimental error.

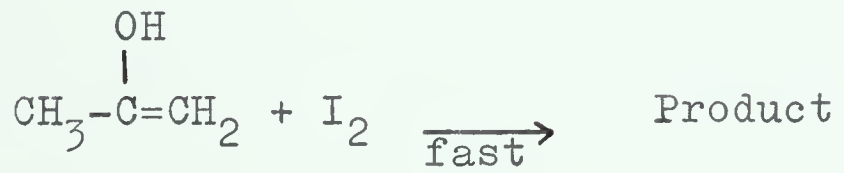
By using the results obtained by other investigators working with ordinary acetone, a kinetic isotope effect was

observed, being 6.0 for oxonium ion, 6.1 for monochloroacetic acid, 6.2 for glycollic acid, 3.4 for acetic acid, 3.7 for trimethylacetic acid and 3.2 for acetate ion, 3.2 for trimethylacetate ion, 1.2 for monochloroacetate ion and 1.0 for glycollate ion.

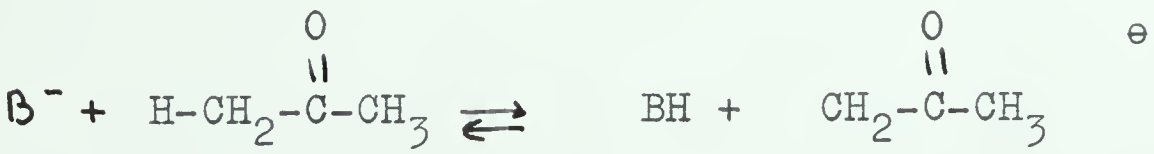
A reconciliation of the kinetic isotope effect with various mechanisms for the reaction is attempted. It would seem that the most probable mechanism for acid catalysis is:

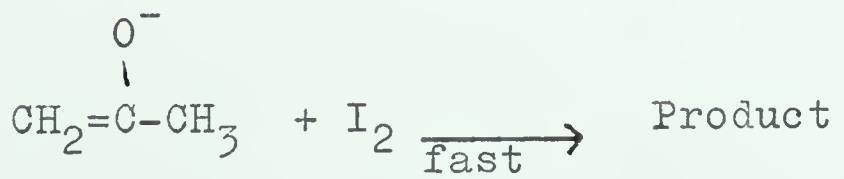




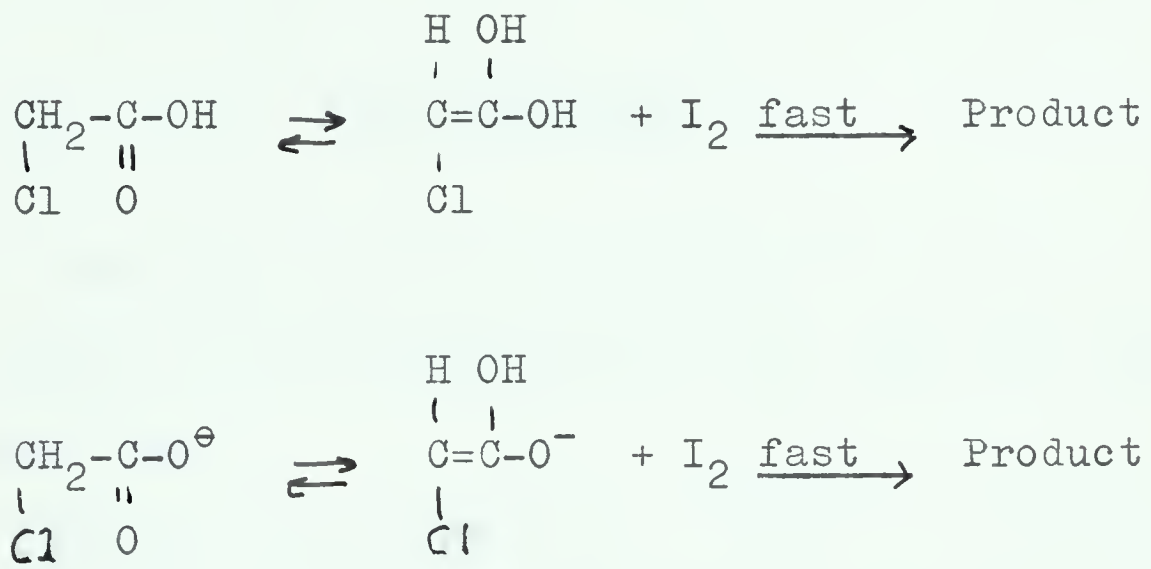


while for basic catalysis:





In the reactions of deuterated acetone catalyzed by the monochloroacetic monochloroacetate pair as well as the glycollic acid glycollate pair, there appears to be a detectable competitive reaction:



ACKNOWLEDGEMENT

The author is deeply indebted to Dr. S. G. Davis, without whose guidance this work could not have been undertaken.

Thanks are extended to the National Research Council for the financial support during the past two summers.

LIST OF FIGURES

A STUDY OF THE KINETICS OF THE IODINATION OF DEUTERIZED ACETONE CATALYZED BY ACIDS AND BASES

INTRODUCTION

The kinetics and mechanisms for the halogenation of ketones have been the subjects of much investigation from the turn of the century to the present day. The possibility that the overall reaction has for its initial phase the changing of the keto $-\overset{\overset{O}{\|}}{C}-\overset{|}{C}-\underset{H}{|}$ to the enol $-\overset{|}{C}=C-\underset{OH}{|}$ was investigated by A. Lapworth (14) in 1904. Kurt Meyer's method (19) for quantitatively determining the amount of enol shed much light on the existence of two distinct skeletal species, for the keto form will not react, while the enol quickly absorbs halogen. Any study of halogenation kinetics is in reality a study of the rate of enolization, as all succeeding steps are rapid compared with enol formation. Lapworth also was among the first to show that the conversion from the keto to the enol forms is the rate determining process. This conclusion was drawn from the facts that the rates of iodination and bromination were equal, and that the overall rate was not dependent upon the relative quantities of bromine or iodine present. In addition, he found that the overall rate was increased by the addition of small amounts of mineral acids. It was not until a few years later that Dawson (7) showed that the reaction was catalyzed

not only by the H_3O^+ species but also by the undissociated acid and the anion. This duality was first reported in the literature by Johnson and Acree (1) who were working on certain catalyzed rearrangements of cyclic structures at the time, but it was Dawson who first made attempts to evaluate the catalytic constant due to the acid, thus making the study a quantitative one.

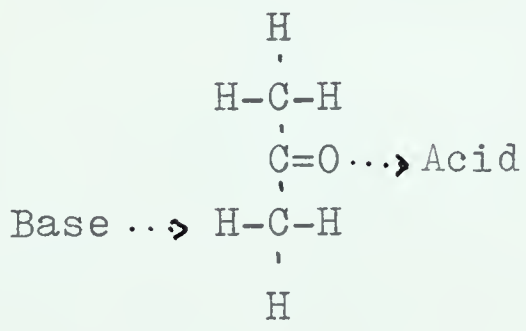
Since the halogenation is catalyzed by H_3O^+ and OH^- ions, it would seem that the preliminary step does involve a proton shift, and any species facilitating proton addition (acid) or proton removal (base) should catalyze the reaction. Certain workers (11, 18) have noticed anamolous behavior concerning the simultaneous action of acid and base on the substrate. Perhaps one of the most outstanding instances of this concerted action was the one reported by Lowry and Faulkner (17), who noticed that while neither pyridine alone (acceptor of protons) nor cresol alone (proton donor) would catalyze the mutarotation of tetramethylglucose, the two acting in conjunction quickly rotated the plane of polarized light. Other workers have noticed the strange behavior of ketone halogenation in anhydrous media. Thus, Hughes and Watson (11) have shown that in anhydrous chloroform or carbon tetrachloride, bromine disappearance is rather static, but after a certain "lag time", the reaction proceeds rather rapidly. Similar results have been shown by Lowry (15) to occur in the mutarotation of some optically active compounds.

Watson (24) goes on to say that experimental evidence indicates that enolization will occur only when some "outside" species are introduced into the system.

It can be shown by the addition of metallic sodium to an equilibrium mixture of keto and enol forms with the resultant liberation of hydrogen that acetone is an acid. That the enolic tautomer is the more acidic can be seen by considering the molecular orbital picture of the enol.(Figure 1).

It will be noticed that the π orbital of the double bond and the p orbital of the oxygen atom overlap with the resulting spread out molecular orbital embracing the oxygen, carbonyl carbon and α carbon atoms. This allows for a greater separation of charge. Since this is not the case for the keto-form, it seems that the enol will be more easily de-protonated.

A suggestion proposed even before Lapworth's work and discussed by Lowry (15), Ingold (10), Pedersen (20), Swain (21) and others,holds that the prototropy depends upon both an acid (or electrophile) and a base (nucleophile) acting simultaneously on the substrate (acetone) in a "push-pull" fashion.



This theory might explain the need for the "lag-time" in some

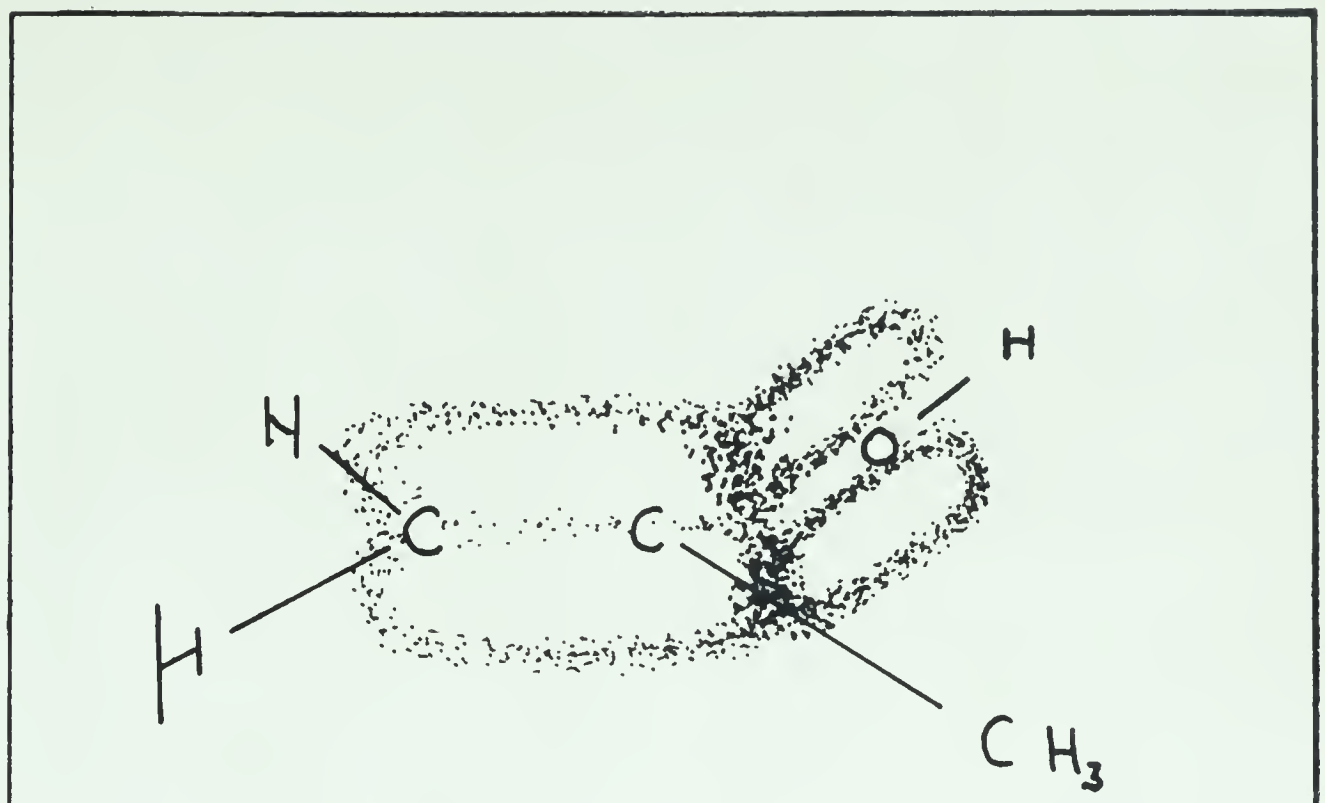
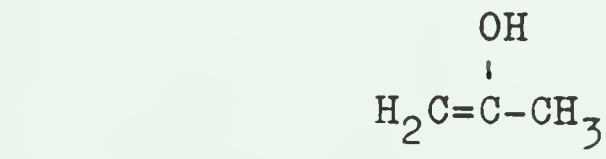


Figure 1

Bonding Orbitals of Enol



of the experiments mentioned earlier. Lowry mentions that this static period may be considered time during which impurities needed for the reaction are being built up. The absence of this period in aqueous media prompted him to suggest that water was here acting as a "complete catalyst", giving rise to the H_3O^+ ion and OH^- ion, whose simultaneous action was needed for the reaction to begin. If a trace of mineral acid is added to the anhydrous system, there is no induction period and the reaction will proceed rapidly. It should be noted here that an acidic medium would favor the existence of the more basic (keto) species, while a basic solution would favor the enol. This is, perhaps, one reason why basic catalysis (especially by OH^-) is usually more effective than acid catalysis. If conditions, e.g., iodine concentration, are favorable, tri-halogen substituted acetone is obtained more readily from OH^- catalysis than H_3O^+ catalysis.

The Isotope Effect

Because of the difference in zero-point energies of hydrogen and deuterium, it is natural for deuterium containing compounds to undergo chemical reactions at a different rate than their hydrogen containing analogs, especially where bonds to hydrogen (or deuterium) are being broken or formed in the rate-controlling step. In many cases the substitution of deuterium for hydrogen has afforded assistance in proposing and verifying certain mechanisms and rate

processes.

The isotope effect (the rate with hydrogen as compared with the rate with deuterium) is most informative about mechanism when it is large (rate with the deutero compound much slower than with the hydrogen one) or when it is small or non-existent (both rates being equal or nearly so). A large effect might mean that a carbon to deuterium bond is being broken or formed in the rate-determining step while a small one would indicate that this is not the case.

It has been shown in classical mechanics that the energy of a bond is a direct function of the vibrating frequencies of the atoms involved in the union. The familiar relationship

$$E = \tfrac{1}{2} h \nu$$

for the zero point energy of a bond

where h = Planck's constant

ν = Frequency of vibration

states for two vibrating systems, the one having the greater frequency will have the greater zero point energy. The two main reasons for the difference in vibrating frequency between hydrogen and deuterium bonds are the free energy differences arising from the different number of sub-atomic particles and the consequent differences in nuclear spin and the like and the more obvious one, the difference in mass. From a typical Morse function curve (Figure 2) drawn for hydrogen (the one for deuterium being identical) it will be seen that the only

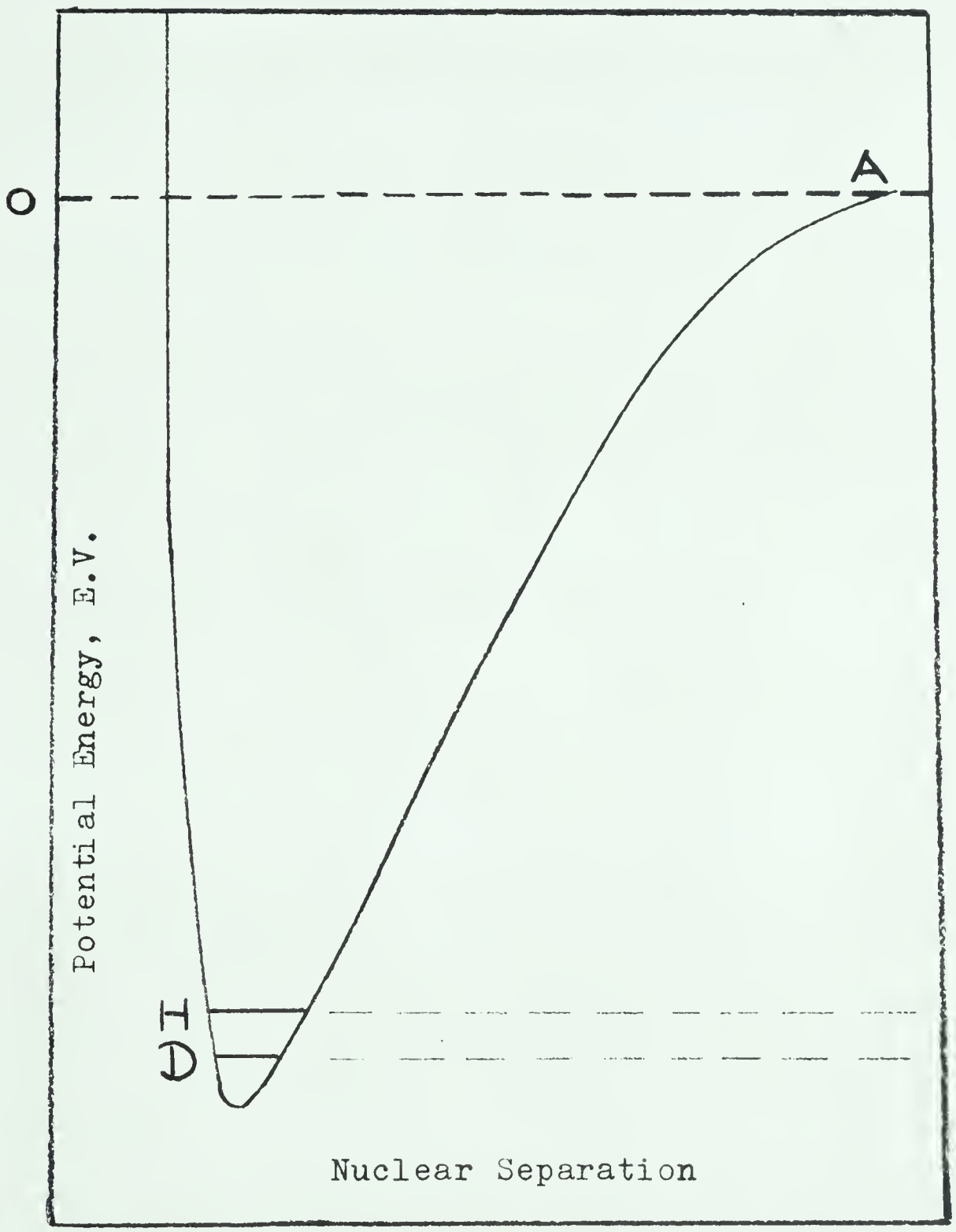


Figure 2

Morse Curve for H-H

place where there is any difference is in the zero-point energy level of the hydrogen and deuterium bond, the hydrogen bond having a higher energy level. This difference in energy levels may be attributed to the differences in masses, which affects the vibrational frequency and thus the bond energy. This difference is of the order of 1.5 k-cal per mole.

The significance of the differences in zero-point energies lies in the realization that bond rupture occurs only when the attractive forces of the bonds do not exist, that is, when the energy of the bond approaches zero (A) in Figure 2. Since the zero-point energy level of hydrogen is higher than for deuterium, more energy would be needed to break the deuterium bond by an amount

$$E_H^\circ - E_D^\circ$$

Activated Complexes: maximum and minimum isotope effects.

Figure 3 represents the familiar energy vs. reaction parameter plot used for the explanation of rate processes.

According to this scheme, for any reaction to take place a certain "energy of activation" is needed which will raise the reactants to a higher state of potential energy, or a so-called activated complex. The position and form of

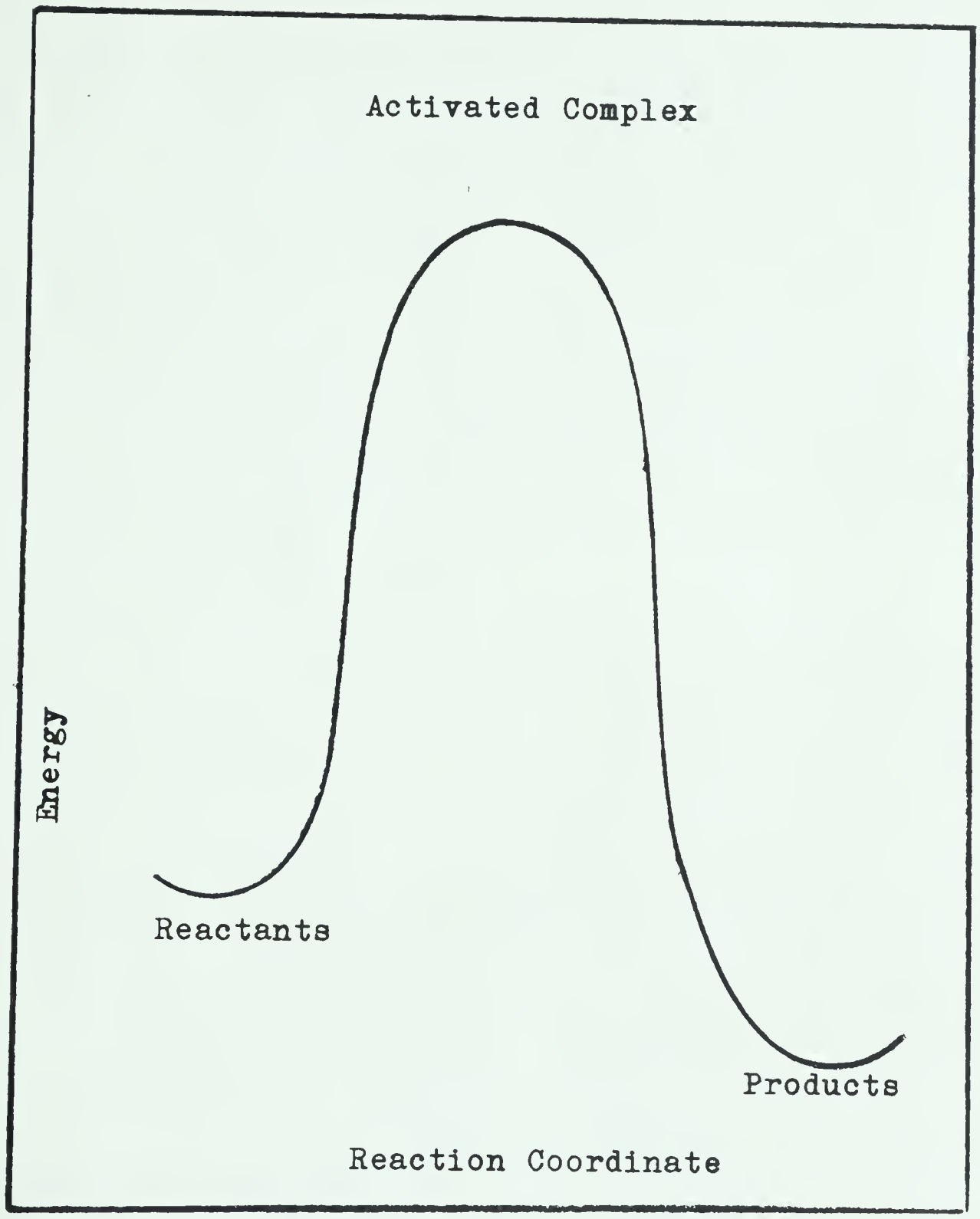


Figure 3

Energy-Reaction Parameter Plot

the activated complex determines the ease with which the stable potential energy minima of the products may be reached. Assuming that the Arrhenius equation relating specific rate constants to activation energies holds, the difference in zero-point energies will bring about the largest differences in rates. An immediate objection might be raised that the activated complex itself contains a certain difference in zero-point energy levels when referring to the hydrogen complex and the deuterium one. Although this is so, it is also true that the proton or deuteron in the activated complex will be less firmly bound than in the reactant compounds, so that the frequencies and therefore the zero-point energies will be very small and the difference between zero-point energy levels will be very slight.

If the activated complex is one in which a hydrogen bond is being broken or formed the use of a deuterium substituted analog will give information concerning the relative strengths of the bonds in the activated complex. By using Bigeleisen's and Wiberg's mathematical description of isotope effects, much can be said about bonding in the activated complex, especially where either large isotope effects or small ones occur (4, 25).

Mathematical Approach

According to Eyring's theory of absolute rates, the speed of a reaction depends upon both the concentration of the activated complex and the ease with which it passes over the potential energy barrier. The specific rate constant may be expressed as

$$k = \kappa \frac{C^*}{C_A C_B} \left[\frac{kT}{2\pi m^*}\right]^{\frac{1}{2}} \cdot \frac{1}{\delta} \qquad (1)$$

where k = specific rate constant

κ = transmission coefficient

m^* = effective mass of the complex

δ = Length of potential energy barrier

k = Boltzmann's constant

C = concentration

Writing a similar expression for a deutero-activated complex and dividing Equation 1 by it, one arrives at

$$\frac{k_H}{k_D} = \frac{\kappa_H \, C_{H^*} \, C_D \, C_{iodine}}{\kappa_D \, C_{D^*} \, C_H \, C_{iodine}} \left[\frac{m^*_D}{m^*_H}\right]^{\frac{1}{2}}$$

where the last term includes the respective masses of the deuterium complex and the hydrogen complex. The transmission constants for the deuterated and hydrogen complexes are nearly identical, as are the concentrations of the other reactants in the system and the lengths of the respective potential energy barrier peaks. Cancelling, then, leaves

$$\frac{k_H}{k_D} = \frac{C_{H^*} \, C_D}{C_{D^*} \, C_H} \left[\frac{m^*_D}{m^*_H}\right]^{\frac{1}{2}}$$

Replacing the concentration terms by their corresponding free energy terms, we arrive at

$$\frac{k_H}{k_D} = \frac{K_1 \, f^*}{K_2 \, f^*} \left[\frac{m^*_D}{m^*_H}\right]^{\frac{1}{2}} \qquad (2)$$

where K_1 and K_2 are the respective equilibrium constants for the activated complexes and the reactants. The free energy terms are evaluated by relating them to the partition functions, finally reducing to

$$f = \frac{S_H}{S_D} \prod_i^{3n-6} \frac{u_i}{u_i + \Delta u_i} e^{\frac{\Delta u}{2}} \frac{(1-e^{-(u_i + u_i)})}{1-e^{-u_i}} \qquad (3)$$

where S = symmetry numbers

$$u_i = \frac{h\nu}{T}$$

$$\Delta u_i = \frac{h}{k T} (\nu_{iH} - \nu_{iD})$$

A relation similar to Equation 3 holds for f* (5). It is usual to assume that the other (non-reacting) bonds are unaffected by the reaction, thus simplifying calculations. Since the region of the potential energy surface near the energy barrier defies measurement, one can usually calculate only the minimum isotope effect. As mentioned before, this would correspond to no bonding in the activated complex. In this instance, f* of Equation 2 may be set equal to unity and one may rewrite this equation as

$$\frac{k_H}{k_D} = \left[\frac{m^*_D}{m^*_H}\right]^{\frac{1}{2}} \cdot \frac{h\nu_D}{h\nu_H} \cdot e^{\frac{(h\nu_H - h\nu_D)}{2RT}} \cdot \frac{1 - e^{-h\nu_{H/RT}}}{1 - e^{-h\nu_{D/RT}}}$$

where the energy term ($h\nu$) is in calories $mole^{-1}$. The last term may be set equal to 1 below 500°C. Since the hydrogen

atom vibrates $\sqrt{2}$ times faster than a corresponding deuterium bond, the mass factor, i.e. $\left[\frac{m^*_D}{m^*_H}\right]^{\frac{1}{2}}$, which has a numerical value of $\sqrt{2}$ cancels with it, leaving only

$$\frac{k_H}{k_D} = e^{\frac{(h\nu_H - h\nu_D)}{2kT}}$$

At higher temperatures, for example $h\nu_D \rightarrow h\nu_H$, while $e^{\frac{(h\nu_h - h\nu_D)}{2kT}}$ approaches unity, and again the last term will cancel, leaving only the mass factor, which would have a value of $\sqrt{2}$. This is the limiting case of the low isotope effect, corresponding to weak bonding in the activated complex.

O. Reitz (22, 23) has previously undertaken the study of kinetic isotope effects in the study of the bromination of acetone catalyzed by various weak acids and their corresponding anions in aqueous solvents, both H_2O and D_2O, finding an isotope effect 7.7 for both acid and base catalyzed halogenation of acetone as well as a ratio of $\frac{k_{in\ D_2O}}{k_{in\ H_2O}}$ of 2.3 for the catalyzed halogenation in water and heavy water, which effect it is felt is due in no small part to the different solvation properties of D_2O and H_2O.

The Bronsted Catalysis Relation

Since the mechanism for the overall halogenation

involves proton transfer it can be assumed that the specific rate constants may be related to the acid dissociation constants of the various acid catalysts by the Bronsted relation (6),

$$\frac{ka}{p} = G_A \left(\frac{qKa}{p}\right)^{\alpha}$$

Likewise, for the anion of the acid

$$\frac{k_B}{q} = G_B \left(\frac{p}{qKa}\right)^{\beta}$$

where k = catalytic constant

α, β, G = constants

P and q are statistical factors allowing for application of the Bronsted relation to polycarboxylic acids in bases. Since all the acids and bases studied in this work are monocarboxylic p and q are both equal to unity.

α and β have values ranging between the theoretical limits of zero and unity. Depending on the magnitude of these constants one can usually assign approximate percentage values of the overall rate due to solvent, oxonium ion and undissociated acid, or solvent, hydroxide ion or dissociated acid for basic catalysis.

Thus, if the overall rate is given by:

$$k_{total} = k_{H_3O^+} \left[H_3O^+\right] + k_{H_2O} \left[H_2O\right] + k_{HAc} \left[HAc\right] \qquad (1)$$

and one assumes a Bronsted relation for each of the species mentioned in Equation 1, the following may be written

$$k_{H_2O} = GK_{H_2O} \qquad k_{H_3O^+} = GK_{H_3O^+} \qquad k_{HAc} = GK_{HAc}$$

At a pH value of about 4.7, taking the percentage of each individual term in (Equation 1) as compared with k_{total}, one would find:

TABLE I

	Percentage of Rate Due To:		
α	H_3O^+	H_2O	HAc
0.0	Negligible	Predominant	Negligible
0.5	Appreciable	Negligible	Appreciable
1.0	Predominant	Negligible	Negligible

A similar arrangement may be drawn up for a consideration of β values.

This is intended only as a qualitative guide, since the acids in question (H_2O, H_3O^+ and HAc) are not closely enough related to follow exactly the Bronsted relation.

EXPERIMENTAL

Apparatus

The reaction between acetone and iodine was followed colorimetrically using a Beckman Model "DU" quartz prism spectrophotometer and pyrex cells. All measurements were taken at wavelength 460 mμ, near the peak of the ordinary iodine absorption curve. The basis for this method is that the characteristic yellowish-brown solution of acetone and iodine gives way to the colorless iodide and iodoacetone (CH_3COCH_2I) neither of which absorb at 460 mμ. All reactions (except the fast H_3O^+ catalyzed one) were carried out in sealed pyrex cuvettes, as shown in Figure 4. This was done to minimize the volatilization of iodine. To accommodate the added length of the cuvettes, the spectrophotometer cell compartment was fitted with a light-proof adaptor, which fitted the cell housing tightly. Since many of the measurements lasted for several weeks all reaction mixtures were kept in a thermostatically controlled bath at 25° ± .05 C, rather than in the cell compartment itself, whose temperature could be maintained only at 25° ± 1. The iodine concentration of all samples ranged from 9.73×10^{-3} to $.25 \times 10^{-3}$ moles I_2/liter. For hydronium ion catalysis both a saturated (at 20°C) solution of iodine and one of 4×10^{-3} molar I_2 were used.

The light and heavy acetone were admitted to the iodine-buffer solution by means of a calibrated "E-Gold-Line"

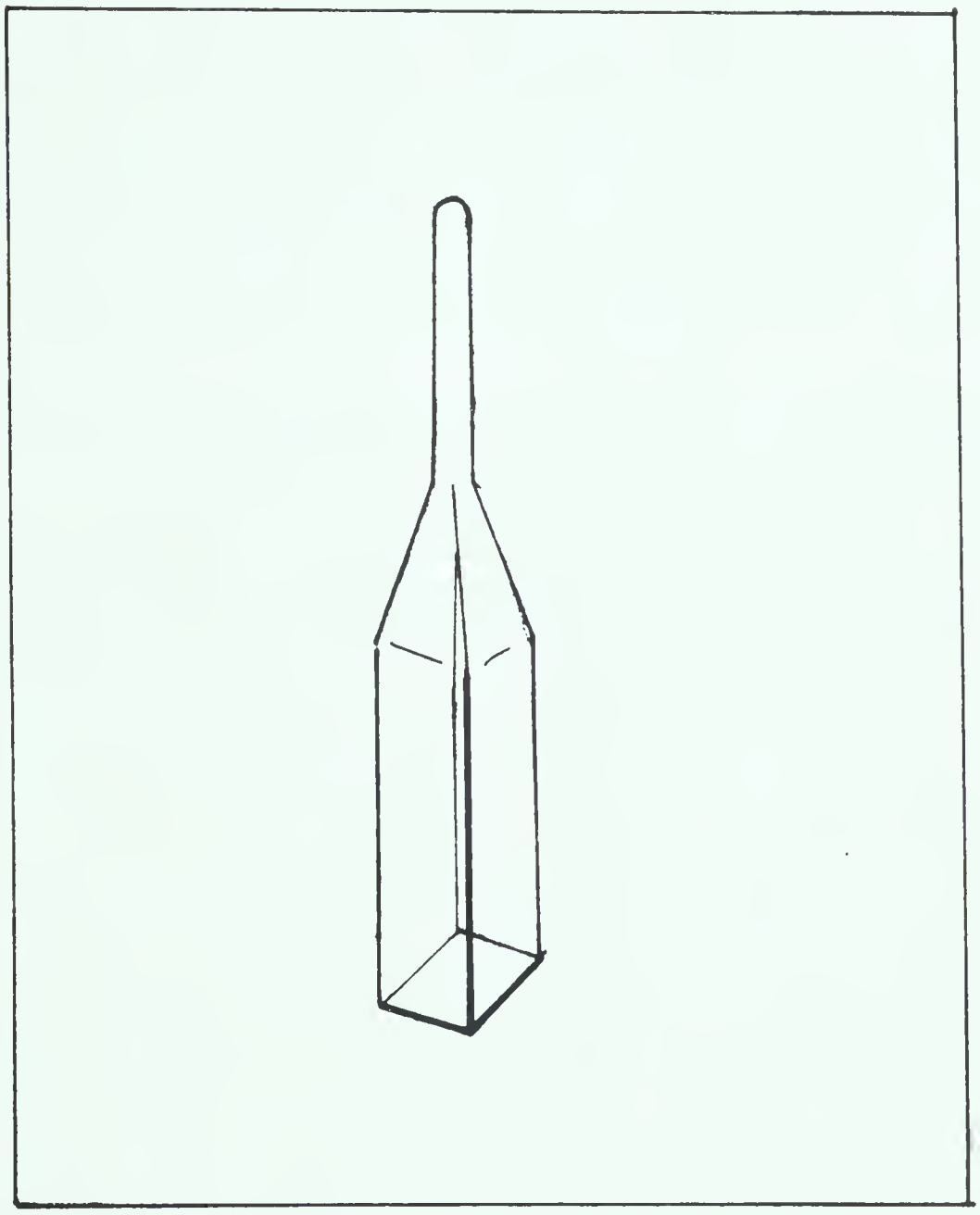


Figure 4

Pyrex Reaction Vessel, Sealed Tip

.1 cc micro-pipette. The mixture, after being thoroughly mixed, was slowly admitted to the reaction cuvette by means of a glass barrel hypodermic syringe and four-inch needle. All bubbles that might have interfered with light transmission were carefully removed. The long tip was drawn off by an oxygen torch in the middle, rather than being collapsed at the tip, so that no gas or oxygen could be admitted to the solution undergoing test. The flame was directed far enough from the reaction mixture so that the temperature of the solution itself was not materially affected.

Materials

The light hydrogen acetone used was Eastman-Kodak spectro grade from a previously unopened bottle. Heavy acetone, 99.5% pure, was transferred under vacuum to a ground glass stoppered container just prior to use. After removal from the sealed shipping vessel, the heavy acetone was stored in a small, silica gel filled, completely air tight dessicator. The acids (used as catalysts) were all pure commercial specimens, all of which were titrated with appropriate standard base and indicator and found to have a minimum purity of 99.7 for glycolic acid, 99.8 for monochloracetic acid, trimethyl acetic acid and acetic acid. The sodium salts (basic catalysts) were prepared from carbonate free sodium hydroxide, standardized with potassium hydrogen phthalate and phenolphthalein indicator. All acid-base titrations were reproducible to within 2 parts per thousand. The sodium chloride

used as the "inert" salt was analyzed reagent grade, having a purity (dried) of over 99.7%.

All iodine titrations were performed by means of sodium thiosulfate $Na_2S_2O_3 \cdot 5H_2O$, according to the reaction

$$I_2 + 2S_2O_3^{-2} \rightarrow 2I^- + S_4O_6^{-2}.$$

The sodium thiosulfate was standardized using potassium dichromate and an acidified solution of excess potassium iodide

$$Cr_2O_7^{-2} + 6I^- + 14H^+ \rightarrow 2Cr^{+3} + 7H_2O + 3(I_2),$$

the liberated iodine being titrated with thiosulfate and starch indicator. Owing to the unstable character of thiosulfate solutions, restandardization was carried out prior to each titration. Results were duplicated using primary standard grade Arsenious oxide as a further check.

Buffer Composition

The buffer composition for acetic acid - acetate, glycolic acid - glycollate, monochloroacetic - monochloroacetate, ranged from .070 M to .150 M in the basic ion. The acid to base ratio was chosen so that catalysis by H_3O^+ and by OH^- would be small compared to catalysis by the undissociated acid and its conjugate base. A natural consequence of buffer usage would be the absorbance of the traces of HI formed from the main reaction

$$CH_3\overset{\overset{O}{\|}}{C}CH_3 + I_2 \rightarrow CH_3\overset{\overset{O}{\|}}{C}-CH_2I + H^+ + I^-$$

While considerable amounts of H_3O^+ would indeed shift the buffer ratio, the minute quantity formed would not shift it detectably, although the trace amounts of H_3O^+ would autocatalyze the reaction to a marked extent if the buffer were not present.

Two buffer ratios for each acid (corresponding to two different pH values) were used. Sodium chloride was added so that the ionic strength for all solutions would be .150. The figures for the acetic acid - sodium acetate buffers are shown in Table II.

TABLE II

$$\text{Ratio (R)} = \frac{\text{Acetic Acid}}{\text{Sodium Acetate}}$$

R = 1 pH = 4.7

Sodium Acetate	Acetic Acid	Sodium Chloride
.150 M	.150 M	—— M
.112	.112	.038
.090	.090	.060
.070	.070	.080

R = .35 pH = 5.2

.150	.052	——
.112	.039	.038
.090	.032	.060
.070	.025	.080

A similar scheme was followed for all other buffers with the exception of the trimethylacetic acid - trimethyl acetate buffer whose anion concentration ranged from .045 to .125 M.

In order to equate optical density measurements with iodine concentration, it was necessary to establish a correlation curve. This was done by dissolving a small amount of iodine in pure water. A small sample was reserved for transmission measurements while another (measured) portion of the same sample was titrated with standard thiosulfate and starch indicator. All titrations were done as quickly as possible to minimize loss of I_2 through volatilization. Different iodine concentrations were each plotted against their respective optical density readings and the plot was drawn up (see Figure 5). This procedure was repeated several times and excellent agreement was achieved.

Measurement of Rates

Since the specific rate constants for the iodine-(light) acetone reaction using the catalysts mentioned have been calculated before by Bell (19), using a titrimetric procedure, it was thought that these results should be duplicated by the spectrophotometric method as a check on technique.

To each of eight buffers (four of one pH and four of another pH value) a few crystals of resublimed iodine were added. The iodine was allowed to dissolve in a cool, dark atmosphere until the brownish-yellow color of dissolved iodine was fairly strong. The iodine solution was then

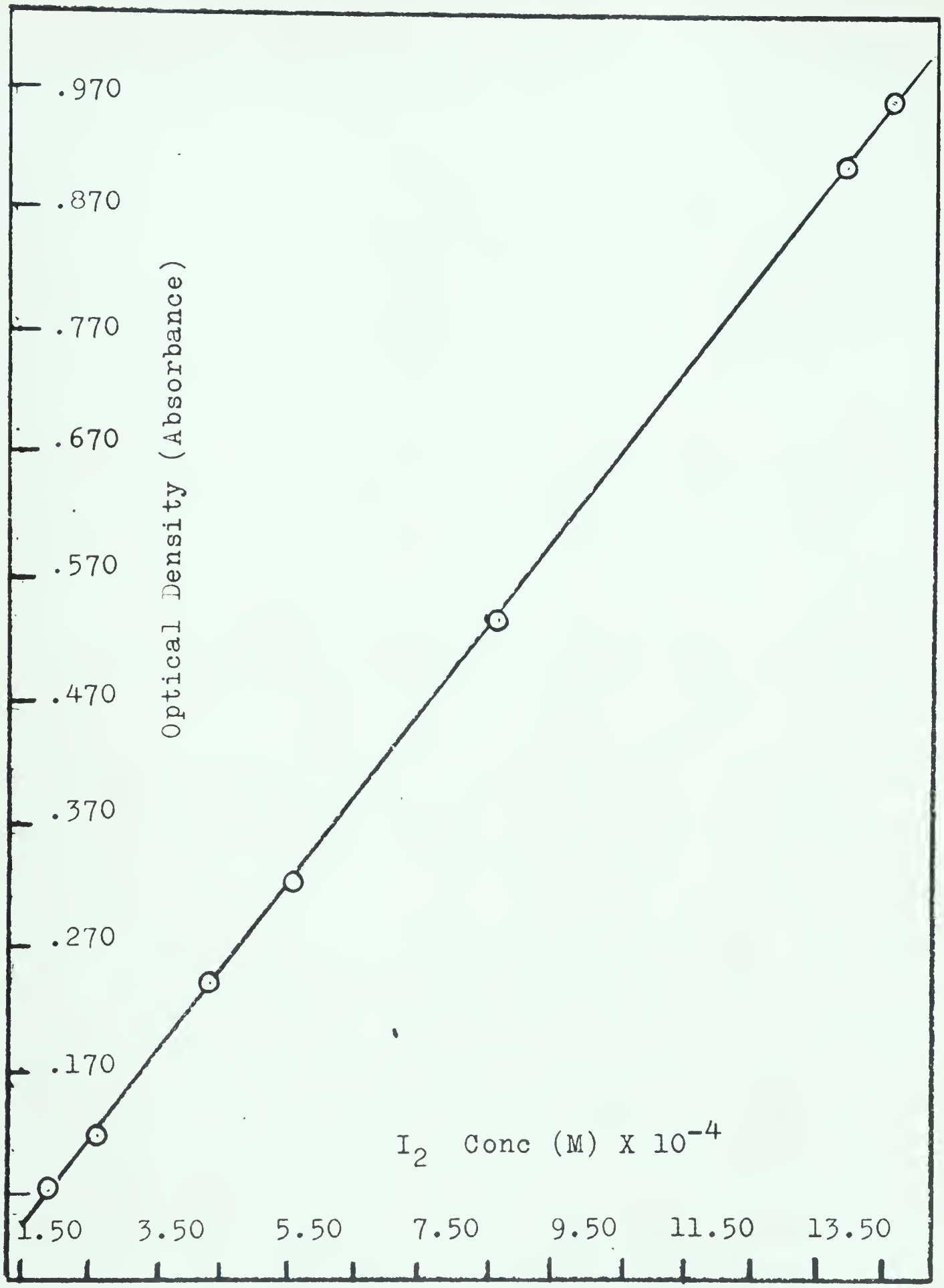


Figure 5

Calibration Curve: Optical Density

Vs. I_2 Concentration

separated from the iodine crystals and was allowed to come to 25°C, before acetone was added. The spectro grade acetone was added by a micro pipette whose capacity for light hydrogen acetone had been determined to be 0.0841 grams $\pm$ 0.0005 in the temperature range 22° to 26°C. The acetone was drawn past the mark and the tip stroked with cotton until the level of the acetone was at the constriction (i.e. .1 cc) point. The acetone was then admitted to exactly 20.00 cc of iodine-buffer solution, giving a final volume of 20.01 cc of reaction mixture, corresponding to an initial acetone concentration of 7.08×10^{-2} mole/liter. The pipette was flushed out four times with small portions of the solution to insure complete removal of all the acetone from the pipette. After the solution had been thoroughly mixed and the time of addition noted, about 3 cc was placed into a cuvette, swirled to insure a good rinsing and discarded. Then, a fresh 4 cc portion was "injected" and readings were begun. At least two samples (i.e. two cuvettes) were reserved for each reaction mixture. After each reading the cuvettes were placed in the bath. The time intervals between readings varied with the concentration and effective power of each particular catalyst used, being as frequent as once every three hours for the light acetone reaction catalyzed by the acetic acid - sodium acetate pair to about once every 50 hours for the deuterated acetone run catalyzed by the monochloroacetic acid - sodium monochloroacetate buffer. For catalysis by the H_3O^+ species without

buffers, the main body of the reaction was completed within 60 minutes, necessitating a reading on the average of every five minutes.

The mode of spectrophotmeter operation was that recommended in the manual supplied with the instrument, using the tungsten filament lamp. Best results were found using a slit width between .08 and .1 mm. Measurements were taken with only one "unknown" in the cell compartment, although there was room for two more. Several determinations were made on each sample, care being taken to balance the dark current and sensitivity galvanometer before each reading. In the majority of cases, the second reading was identical with the first, but where there was deviation additional readings were taken until precise results were obtained. Because of the heat generated by the tungsten lamp, the cell compartment was cooled by the cooling attachment provided by the manufacturer. By using this arrangement, the temperature of the cell compartment rarely exceeded 26°C, while without the coil in operation the temperature would quite readily exceed 30°C.

Since the optical density scale is logarithmic, the initial concentrations of iodine were limited to give an initial reading below .600 optical density unit for increased accuracy when taking measurements. A typical run of optical density units (I_2 concentration) vs. time is shown in Figure 6.

In a great many cases the first and sometimes second points were not on the straight line drawn through the remaining points. It is now thought that this occurs because the

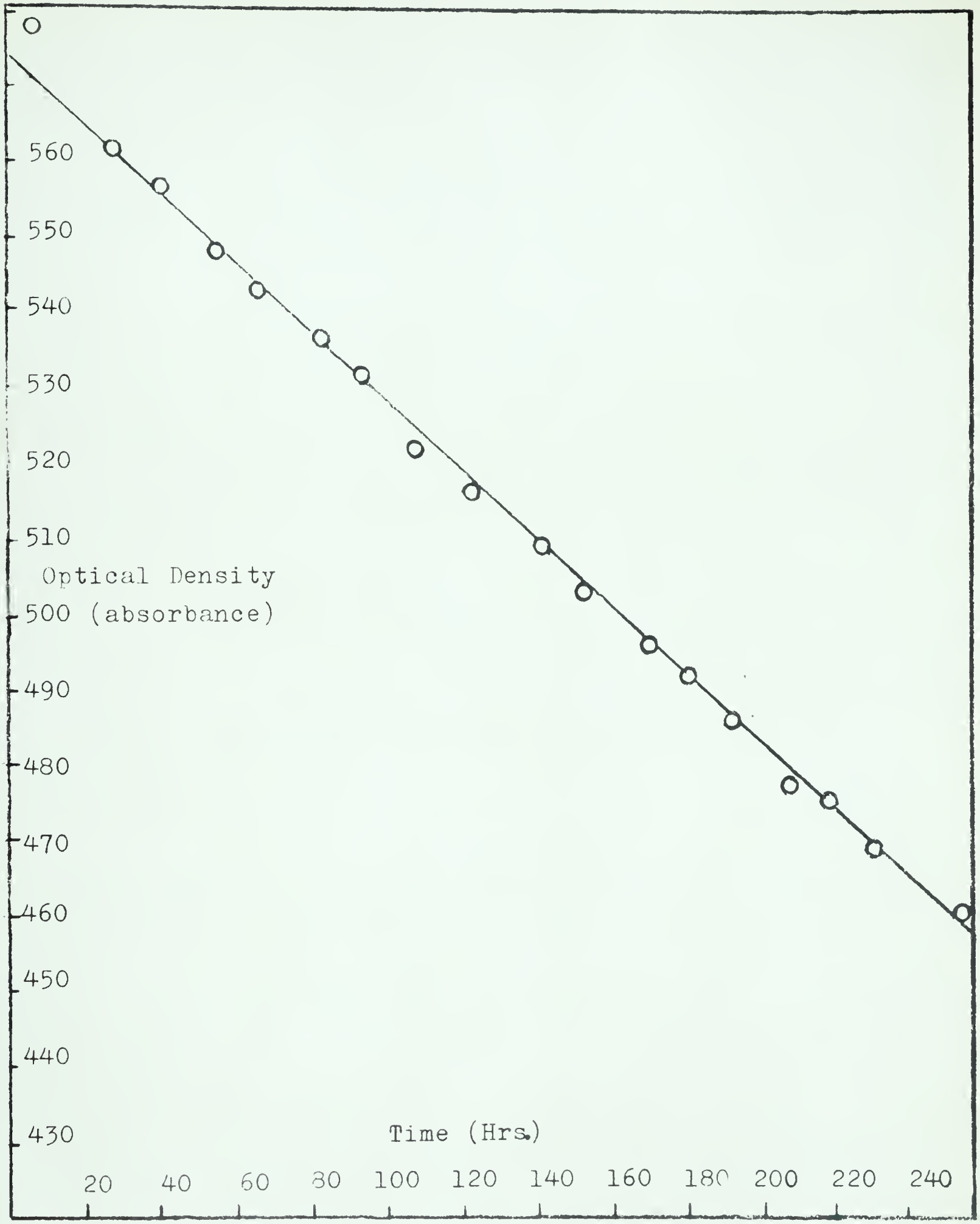


Figure 6

Optical Density Vs. Time

Glycollic Acid-Sodium Glycollate Buffer

iodine volatilizes until such a point that the vapor in the stem is in equilibrium with the pressure exerted by the iodine still in solution. Hence, the initial rate (as determined by the first two points) would seem very fast, but would revert to a slower disappearance once equilibrium was attained. Moreover, since the deuterated acetone was only 99.5% pure, it would be expected that the remaining .5% which probably consists mostly of light acetone would react more quickly with I_2 than the heavy fraction would. This might also add to the fast initial I_2 disappearance observed.

The procedure for the remaining buffer pairs was essentially the same, with the exception of the trimethylacetic acid - timethylacetate buffer whose solutions were made up by weight from trimethylacetic acid (titrated and found to be 99.75% pure), while the rest of the buffers were prepared from aqueous solutions of the weak acid.

The Blank Run

Since there might be loss of I_2 (besides volatilization) by some side reaction between iodine and the various species (H_2O, H_3O^+, OH^-, etc.) which are present in the reaction system (although the concentration of OH^- is very low) it was thought best to run blanks, consisting of the buffer solutions and iodine as well as a solution of pure water and iodine. That there is some side reaction (whether physical or chemical) was shown by noticing a small decrease in optical density with time in two of the buffer solutions under test.

These blank determinations revealed a disappearance of I_2 that would account for perhaps more than 10% of the overall reaction.

Catalysis Due to the H_3O^+ Ion

Several runs were performed to determine the catalysis due to H_3O^+ (i.e., determination of $k_{H_3O^+}$) using both heavy and light acetone. In each case the concentration of H_3O^+ was .01 M, prepared from standard HCl solution, while the acetone concentration was the same as that used in the buffer measurements. Because of the speed of the reaction, and the danger that iodine volatilization would mask the results, the entire cuvette including the short tip was filled with the reaction mixture. The solution was then protected from the atmosphere by means of a very tight-fitting rubber stopper, thus leaving no vacant space at all in the cell. All materials used in the determination were placed in the constant temperature bath and were mixed only after reaching 25°C. The resulting curves of iodine concentration were good linear plots, with practically no scattering. Several other runs were undertaken, one using a concentration of .150 molar in sodium chloride, one with a potassium iodide concentration of .150 M, and one with no added salt. The reason for the potassium iodide run was to observe any difference in halogenation rates when the iodine was mainly present as the tri-iodide complex.

$$I_2 + I^- \longrightarrow (I_3)^-$$

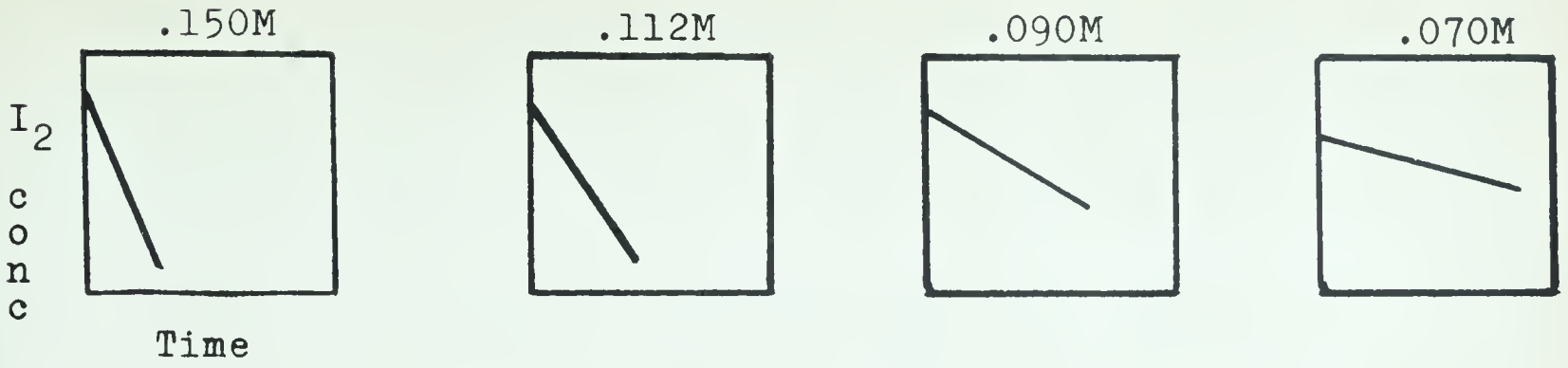
This is also an excellent way of decreasing iodine volatilization (13). Results showed that the three mixtures gave agreeable results within the limits of experimental error (better than 5%), indicating no effect by the added salts.

Mathematical Considerations

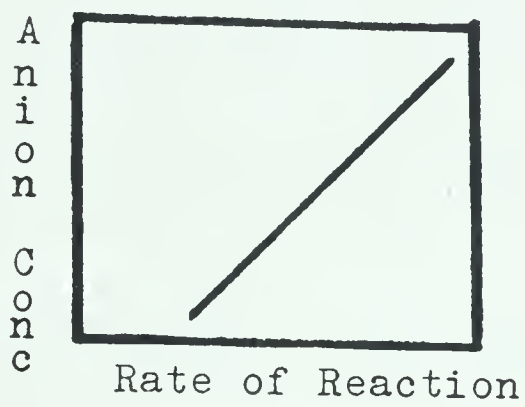
The method used in outlining these mathematical considerations is essentially the same as that applied by Bell (3). By using this method it is unnecessary to know the exact dissociation constants of the weak electrolytes used, especially since this "constant" is increased with increasing ionic strength. The very use of a buffer pair as catalysts keeps the H_3O^+ and OH^- ion concentration constant. By changing the relative amounts of weak acid and its base but still keeping the ratio constant, one changes the effective concentration of catalyst while keeping the pH the same. Thus, one would expect the rate of disappearance of iodine to diminish upon decrease of the amount of weak acid and anion used. For each pH ratio (corresponding to four different catalyst concentrations) four plots may be drawn, as shown schematically in Figure 7.

If one now plots the rate of disappearance of iodine (rate of reaction) vs. the concentration of basic anion (i.e. the slopes of the plots shown in "A" of Figure 7, "B" is obtained. Repeating the entire sequence, but using a different buffer ratio (and thus a different pH value), one

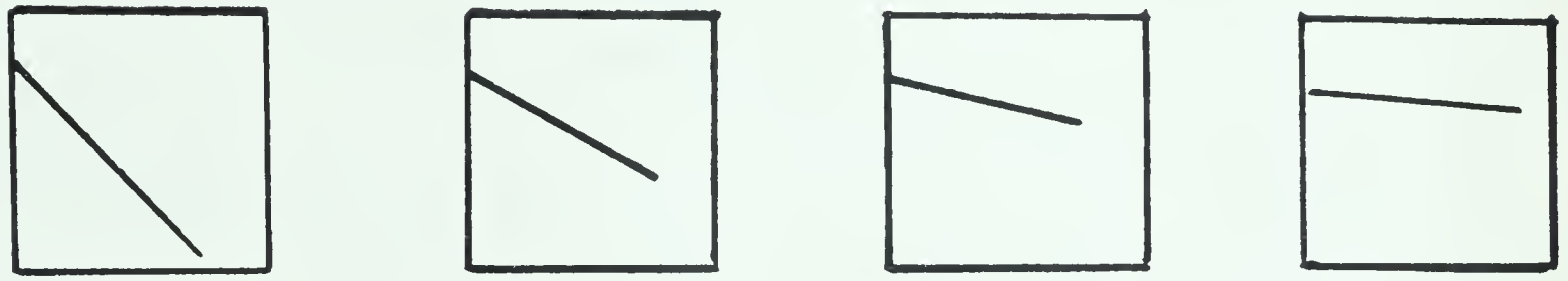
"A"



"B"



"C"



"D"

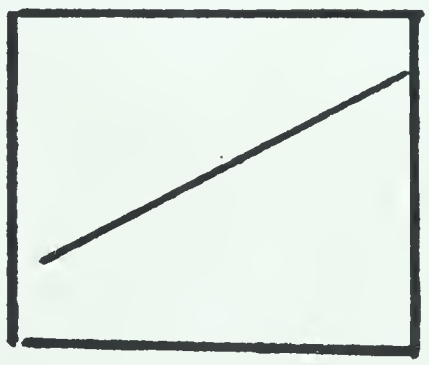


Figure 7

Rates as Functions of Catalyst Concentrations

arrives at the analogous plots "C" and "D". Thus, the rate of reaction as a function of catalyst for two different pH values is obtained. If the general case may be represented as

$$v = k_{H_2O} [H_2O] + k_{H_3O^+} [H_3O^+] + k_{OH^-} [OH^-] + k_{Anion} [Anion] + k_{Acid} [Acid]$$

where v = overall rate of reaction ;

then

$$v = v_0 + k_{Anion} [Anion] + k_{Acid} [Acid] \qquad (1)$$

where $v_0 = k_{H_2O} [H_2O] + k_{H_3O^+} [H_3O^+] + k_{OH^-} [OH^-]$,

v_0 being constant for a given pH.

Rewriting Equation 1

$$v = v_0 + (k_{Anion} + k_{Acid} \times R) [Anion] \qquad (2)$$

where R = Buffer ratio = $\frac{Acid}{Anion}$.

For the other set of buffers corresponding to a different pH, an equation similar to Equation 2 may be written

$$v' = v_0' + (k_{Anion} + k_{Acid} R) [Anion]$$

Plotting the anion concentration vs. v (as done in Figure 5) would give as a slope

$$(k_{Anion} + k_{Acid} R) \qquad (3)$$

for one pH value, and

$$(k_{Anion} + k_{Acid} R') \qquad (4)$$

for the other pH value.

Thus, equating the respective measured slopes to Equation 3 and Equation 4, two equations with two unknowns, k_{Acid} and k_{Anion}, are obtained. Since this method does not rely on a precise knowledge of acid dissociation constants, and since all reactions were carried out at the same ionic strength, there arises no need for calculating activities, primary and secondary salt effects and the like.

Reproducibility

Although each slope for the disappearance of iodine vs. time may be reproduced to better than 5%, it should be noted that any small error would tend to be magnified when plotting rates vs. catalyst concentration ("B" and "D" of Figure 7.). This occurs because the varying catalyst concentrations are very close together, e.g. .070 M and .090 M, giving rates of iodine disappearance which are likewise close together. Thus, small errors in these determinations would necessarily lead to larger errors in the specific rate constants and finally in the isotope effects quoted, so that these isotope effects should be quoted as being $\pm$ 1 unit.

The catalytic constants for the light acetone reaction catalyzed by acetic acid and acetate ions obtained in this work agree to within 2% of those found by Bell (2,3).

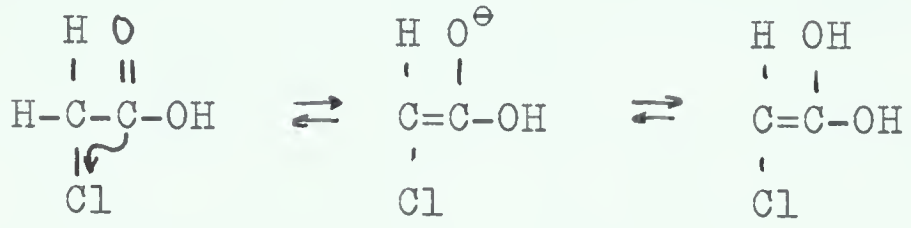
This indicates the accuracy of the spectrophotmetric method even though the initial acetone concentration used in this work was four-fold less than that used by Bell.

RESULTS

The "blank" determinations showed a noticeable disappearance of iodine in the monochloroacetic acid - monochloroacetate buffer mixture as well as in the glycollic acid glycollate one. The acids in each case have higher dissociation constants than acetic and trimethylacetic acids owing to the electron attracting powers of the -Cl and -OH groups. There was absolutely no iodine disappearance in the water solution, while the acetic and trimethylacetic acid buffer solutions showed a negligible decrease when compared with the overall decrease in iodine concentration with the deuterated acetone present. Since the oxidation potential of the iodine-iodide equilibrium is practically independent of hydrogen ion concentration below pH 8 it would seem that the iodine disappearance in the blank runs does not depend on the K_{Acid} of the acids present, but rather upon either redox considerations or the reaction of molecular iodine with the acids or corresponding anions themselves. Because it is doubtful that any of the species involved in the buffer systems in question contain potentials large enough for redox reactions, serious consideration must be given to the latter suggestion - that there is a side reaction between iodine and the acids and bases making up the reacting mixtures.

On studying the structure of monochloroacetic acid and glycollic acid, it becomes apparent that there is an hydrogen adjacent to the carbonyl carbon. That this in itself should case a reaction is doubtful, since the same situation

holds true for acetic and trimethylacetic acids. However, both monochloroacetic and glycollic acids contain inductive groups which might conceivably extend the carbonyl unsaturation to the α-carbon,

thus 

which situation is, in fact, another case of tautomerism. The α-carbon unsaturation now permits a reaction with halogen just as the enol form of acetone does. It is conceivable that the anion form of the acid may also undergo a like tautomeric shift, further hastening the disappearance of halogen. Since the -OH grouping is less inductive than the -Cl atom, tautomerism would be expected to be more pronounced with monochloroacetic acid - monochloracetate ion than with glycollic acid glycollate ion, which was the case. Since these blanks seem to be appreciable (in the neighborhood of 10%) the logical step would be to subtract the blank runs from those due to the reactions with the acetone present. However, the assignment of values for the iodine-acid reaction would in itself require a complete collection of separate data before any quantitative statements could be made. With this in mind, and since the side reaction does not seem overly important, no blank values were subtracted, i.e., the data for these "reactive" acids were treated exactly as those of the "unreactive" or non-competing acids. It is interesting

to note that Reitz (17) also came upon an appreciable blank, but h e attributed this to an impurity in the acid, amounting to about 5% of the overall rate in the case of glycollic acid. The possible side reaction between halogen and mcnochloro-acetic acid was not mentioned, however.

Owing to the concentrations used in this work it is doubtful that auto-catalysis could play an important part in any reaction studied, except perhaps in the run catalyzed by hydronium ion using unbuffered solutions. In this reaction auto- catalysis became apparent after about 1.4×10^{-4} moles/liter of iodine had reacted. Since one mole of iodine removed corresponds to one mole of H_3O formed, auto-catalysis became quite objectionable at a total hydronium concentration of 10.1×10^{-3}M. Due to the very small ratio of undissociated acid to base (2.6×10^{-2}:1) for the monochloroacetic acid- monochloroacetate buffer a change in rates was expected as the buffer ratio shifted, but none was found, at least in the initial stages of the reaction.

The question of auto-catalysis brings to mind the occurrence of the "lag-time" in certain anhydrous media mentioned earlier. Since the simpler krtones contain only a very small fraction of the reactive enol, one would expect an immediate, though undetectable reaction, resulting in the build-up of halogen acid to a point where the reaction would proceed at an ever increasing rate.

TABLE II

Acid Catalysis

Acid	K_A	k in H_6 Acetone	k in D_6 Acetone	Isotope Effect
H_3O^+	55.5	8.3×10^{-3}	1.4×10^{-3}	$6.0 \pm .5$
Monochloro-acetic	1.38×10^{-3}	7.6×10^{-5}*	1.2×10^{-5}	$6.1 \pm .4$
Glycollic	1.54×10^{-4}	19.5×10^{-6}*	3.15×10^{-6}	6.2 ± 1.2
Acetic	1.75×10^{-5}	6.06×10^{-6}*	1.8×10^{-6}	$3.4 \pm .5$
Trimethyl-acetic	9.1×10^{-6}	4.4×10^{-6}*	1.2×10^{-6}	$3.7 \pm .9$

Basic Catalysis

Base	$\frac{1}{Ka} \times 10^{-14}$	k in H_6 Acetone	k in D_6 Acetone	Isotope Effect
Monochloro-acetate	7.2×10^{-12}	3.0×10^{-7}*	2.6×10^{-7}	$1.2 \pm .7$
Glycollate	6.45×10^{-11}	2.6×10^{-6}*	2.3×10^{-6}	$1.0 \pm .1$
Acetate	5.72×10^{-10}	14.6×10^{-6}*	4.6×10^{-6}	$3.2 \pm .4$
Trimethyl acetate	1.10×10^{-8}	24.5×10^{-6}*	7.6×10^{-3}	$3.2 \pm .1$

* Bell and Lidwell (3)

The Isotope Effect

The isotope effects calculated from the experimental data are listed in Table II, together with the specific rate constants for both heavy and light acetone. Rate results are adjusted to give the disappearance of iodine in moles/liter per minute, referred to an acetone concentration of one molar.

Isotope effects at best provide only a qualitative picture of proton (or deuteron) transfer. Large isotope effects, as mentioned earlier, point to weak adherence of the -H bond in the activated complex of the rate determining step, while small isotope effects indicate stronger bonding in the complex. Since it is highly improbable that a C-H bond is not broken in the rate deteemining step, one must assume when confronted with a very small isotope effect that bonding in the activated complex is comparatively strong.

The isotope effects caused by the stronger acids (H_3O^+, monochloroacetic acid, glycollic acid) were practically identical, while those of the weaker ones, although smaller, were also similar. While it is dangerous to suggest that there are separate relations between the group H_3O^+, monochloroacetic acid, glycollic acid on one hand, and acetic and trimethylacetic on the other, it would seem that the most outstanding feature is that the stronger acids have greater difficulty in breaking the -D bond as compared with the -H bond. While this is indeed the case here, it should not be assumed that this occurrence is

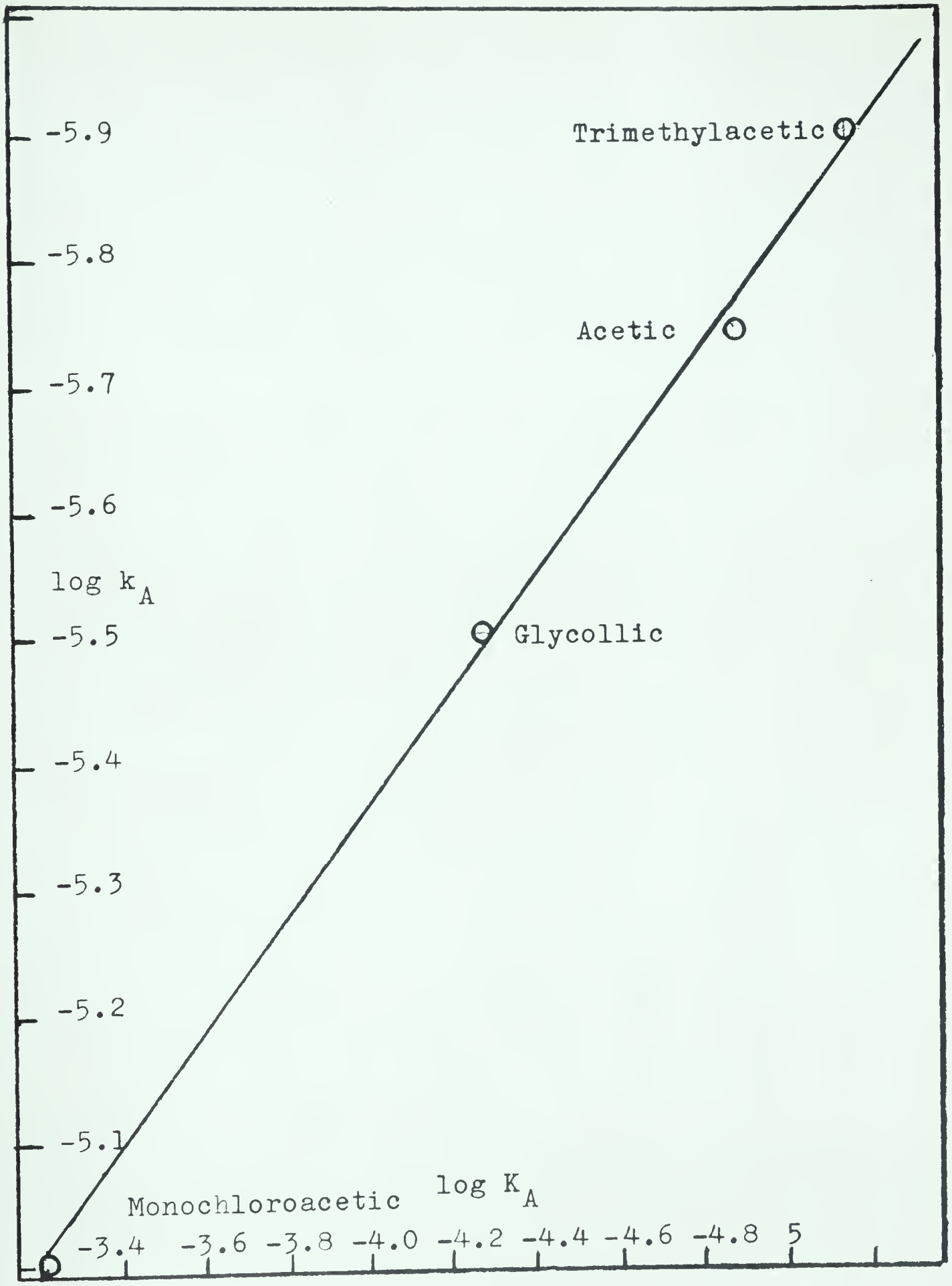


Figure 8

Bronsted Plot: Specific Rate Constant Vs. Dissociation Constant

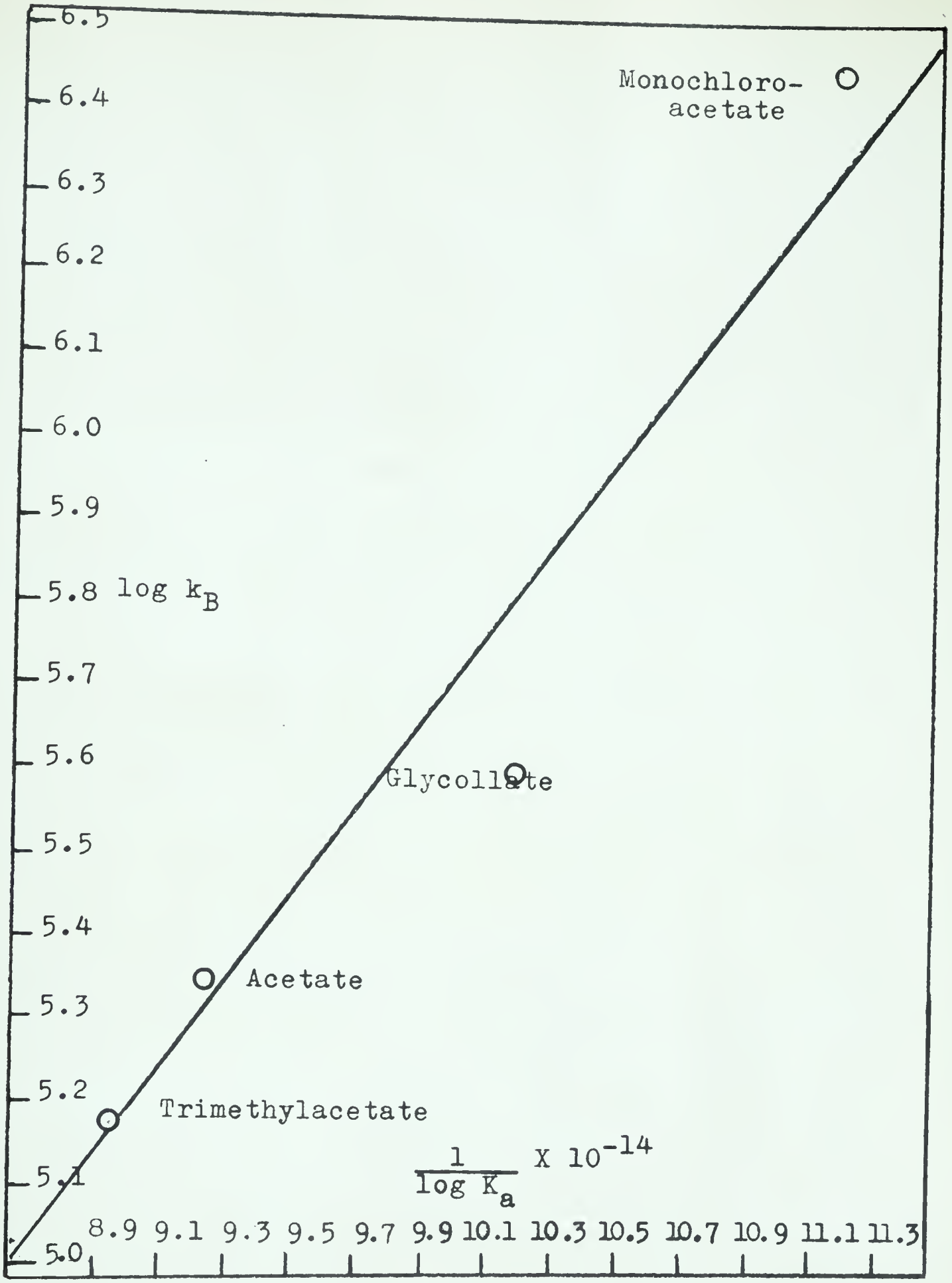


Figure 9

Bronsted Plot: Specific Rate Constants Vs. Dissociation Constant

generally applicable without further evidence. Again, similar isotope effects brought about by catalysts differing in efficiency indicate that the same mechanism is being followed whatever the catalyst, with only the rates differing. This is perhaps another way of stating that whatever the catalyst, the -D bond offers the same relative resistance to bond cleavage as the -H bond. Furthemore, the isotope effects due to the undissociated acid and its corresponding conjugate base cannot be separated, even though separate specific rate constants may be calculated for both the acid and base. Large isotope effects due to undissociated acids and small ones due to the conjugate base seem to go hand in hand. It will be shown later that the rate determining step for the acid catalyzed mechanism involves the deprotonation of the activated complex. Clearly, this proton abstraction is a function of the basic species in the reaction system. With this in mind, two alternatives arise. First of all, it may be the pK_b of the conjugate base which is responsible for the deprotonation, and secondly, the concentration of base itself might be most important. Since all reaction mixtures contained similar amounts of basic catalyst, the latter suggestion must be eliminated. Thus, the acids with the larger dissociation constants and the larger spedific rate constants should give rise to weaker bases and correspondingly smaller rate constants when considering basic cayalysis. This is indeed the case. An immediate objection may be raised that if the deprotonation is

the rate determining step for acid catalysis, then those acids giving rise to the stronger bases (ie. the acids with the lower ionization constants) should give rise to the larger specific rate constants. However, the expression for the formation of enol contains terms only in acetone and general acid and none in general base, indicating no dependence on the conjugate base.

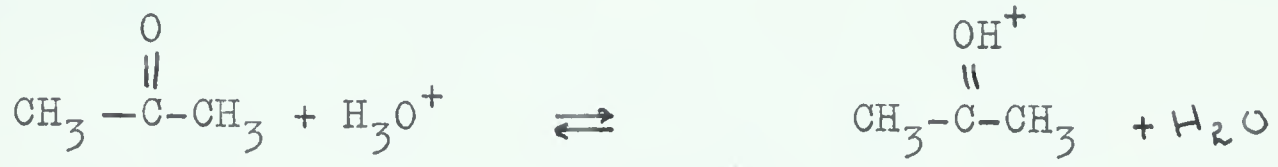
That the isotope effects for basic catalysis seem smaller than for acid catalysis would lead one to believe that the incipiently ionized hydrogen (or deuterium) is so very weakly held in the activated complex that there is really no difference in ease of abstraction and thus in rates. Again, that the isotope effects are close together would point out the sameness in mechanism no matter what the catalyst.

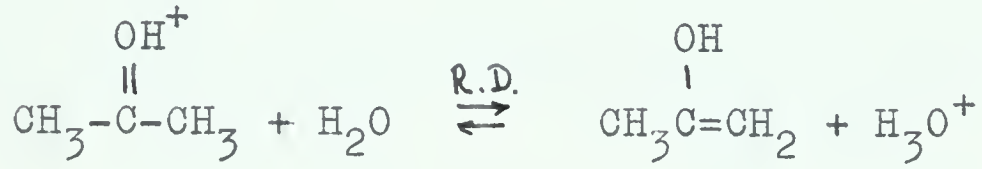
The Bronsted Relation

Atypical Bronsted curve may be drawn for both the acid and base catalyzed reactions (Figures 8&9). The values of α and β are .47 and .53 respectively giving ample evidence once more that the reactions are general acid and base catalyzed. It is interesting to note that the Bronsted curve for the acid portion seems to be a better fit than the basic one. Whether this shows a differing mechanism or a competing reaction peculiar to some of the catalysts and not to the others is difficult to say. If one of the points were far removed from the plot, then it would be safe to assume that there probably would be a side reaction. A Bronsted plot would be expected to show, for example, a wide deviation if the monochloroacetic acid reacted with most of the iodine rather than functioning merely as a catalyst.

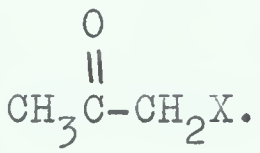
Mechanism: Acid Catalysis

There has been very little modification of Lapworth's original scheme concerning the acid catalyzed halogenation of acetone. This mechanism takes the form:

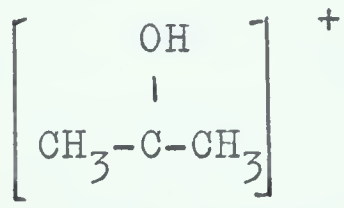




The halogen then reacts very rapidly with the enol, leading to the product



Perhaps the intermediate complex may be better represented by a delocalized charge, represented by the resonating structure

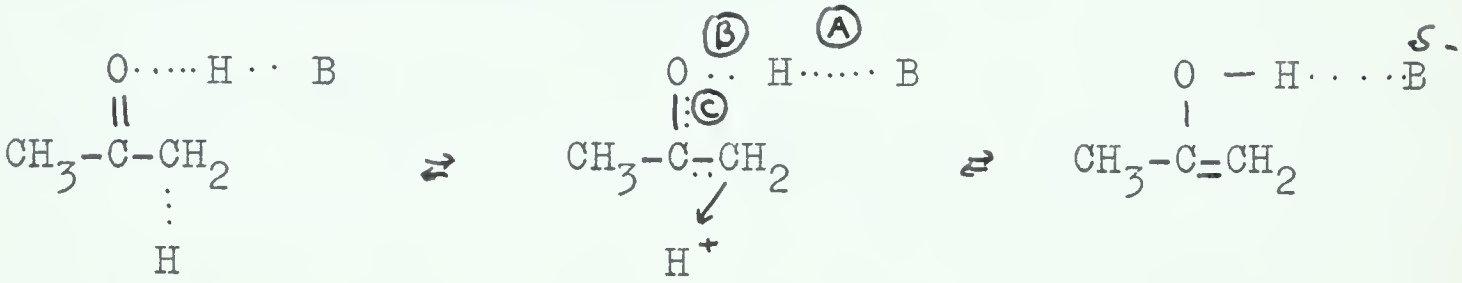


probably in better agreement with the more modern theories concerning molecular orbitals.

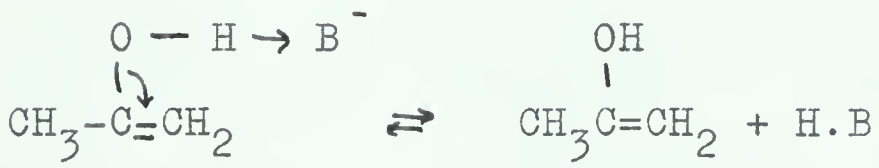
Lapworth's theory is in accordance with all chemical evidence and mathematico - kinetic considerations of deuterium uptake and exchange, optical activity when dealing with certain other ketones, rates of halogenation and the like.

However, throughout the literature there is a distinct tendency to separate "general acid catalysis" from "specific acid catalysis" when mentioning the halogenation of acetone. In the present work these two facets are combined in one mechanism:

where B may be H_2O, acetate, monochloroacetate, etc.



I

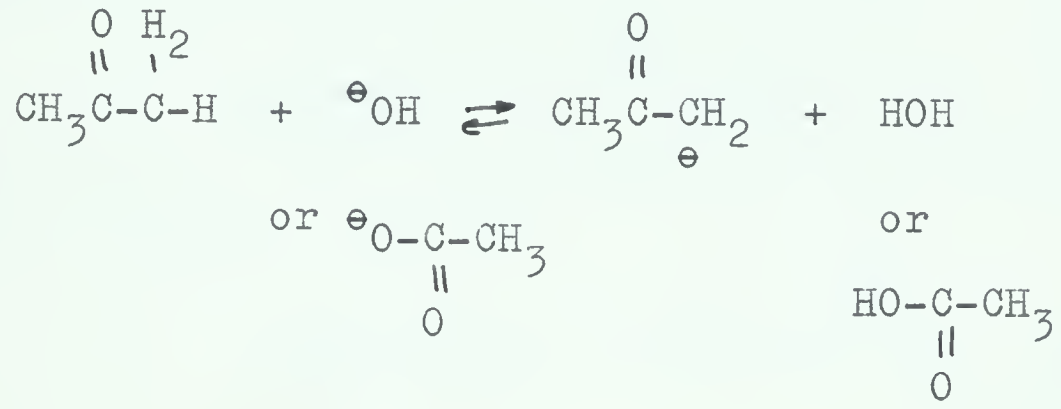


The speed with which the deprotonation occurs would depend on the relative strengths of bonds A and B; if one is strong, then the other of necessity must be weak. In other words, the more displaced (A) the stronger (B), allowing a transfer of electrons from (C), facilitating the removal of a proton in I. This would account for the high k_{Acid} values of H_3O^+, monochloroacetic acid and glycollic acid. Ingold (12) prefers to call the intermediate an "acid

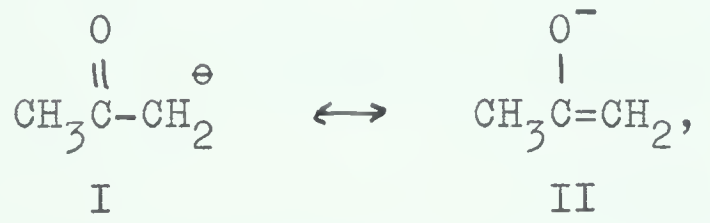
complex" although he doesn't picture the mode of bonding.

Mechanism: Basic Catalysis

The base catalyzed mechanism does not seem to be as complicated as the acid catalyzed one. As mentioned earlier, the α-hydrogen of acetone has definite acidic tendencies. It is quite conceivable then, that the first step in the base catalyzed mechanism would be deprotonation:

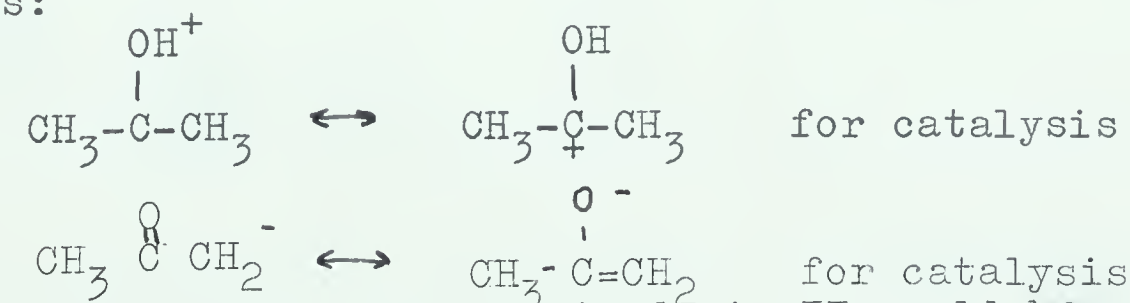


The enolate (or enolide) anion formed would resonate thus:



expected to be the more stable (higher contibuting structure). This intermediate then reacts with halogen to give the mono-substituted product in the fast step.

Perhaps the main reason why catalysis by the hydroxide ion is many fold more efficient than the oxonium ion lies in the relative stabilities of the two intermediate complexes:



where the resonating forms outlined in II would be more easily formed.

In the mechanism proposed in this work it is plausible that for acid catalysis either the protonation of the ketone to form the acid complex or the deprotonation of the α hydrogen(or deuterium) atom might be the rate determining step. If the general case for acid catalysis is

$$HA + CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \leftrightharpoons CH_3-\overset{OH^+}{\overset{|}{C}}-CH_3 + A^-$$

$$CH_3-\overset{OH^+}{\overset{|}{C}}-CH_3 + B \rightarrow CH_3\overset{OH}{\overset{|}{C}}=CH_2 + BH^+$$

one may write for the formation of product:

$$\frac{d[\text{enol}]}{dt} = k_2\left[CH_3\overset{OH^+}{\overset{\|}{C}}CH_3\right][B],$$ if the second step (deprotonation) is the rate determining one. Solving for the intermediate complex:

$$\frac{d}{dt}\left[CH_3cCH_3\right] = k_1\left[HA\ CH_3\overset{O}{\overset{\|}{C}}CH_3\right] - k_{-1}\left[CH_3\overset{OH^+}{\overset{\|}{C}}CH_3\right][A] - k_2\left[CH_3\overset{OH^+}{\overset{\|}{C}}CH_3\right][B]$$

Assuming the steady state approximation, the following obtains--

$$CH_3CCH_3 = \frac{k_1[HA]\left[CH_3\overset{O}{\overset{\|}{C}}CH_3\right]}{k_{-1}[A]+k_2[B]}$$

Substituting this value for the complex in the equation for the formation of product leads to:

$$\frac{d[\text{enol}]}{dt} = k_2[B]\left\{\frac{k_1[HA]\left[CH_3\overset{O}{\overset{\|}{C}}CH_3\right]}{k_1[A]+k_2[B]}\right\}$$

Since k_2 B is very much larger that k_{-1} A, one may write:

$$\frac{d[\text{enol}]}{dt} = k_2[B]\ k_1\left\{\frac{[HA]\left[CH_3\overset{O}{\overset{\|}{C}}CH_3\right]}{k_{-1}[A]}\right\}$$

Utilizing the relationships

$$BH^+ + A \leftrightharpoons HA + B$$

and

$$K = \frac{[HA][B]}{[BH][A]},$$

the final expression may be written:

$$\frac{d[enol]}{dt} = k_1 K [BH][CH_3\overset{\overset{O}{\|}}{C}CH_3]$$

$$= k[BH][CH_3\overset{\overset{O}{\|}}{C}CH_3].$$

This final expression contains a term for general acids and acetone, a result in agreement with observed data. Moreover, if the rate determining step were the protonation of the ketone, a series of ketones of varying pK_b would be expected to show differing rates of halogenation. That this is not the case has been shown by Bell°

The Polymolecular Mechanism

Perhaps the main competition to these unimolecular mechanisms would be the polymolecular one supported by Lowry, Swain and others (8, 16, 21). All attempts to exclude this possibility have been unsuccesful, but it has been shown by Bell (2) that the percentage of the overall rate due to this mechanism is very small, at least for the halogenation of acetone.

Suggestions for further Investigation

Since it has been shown that monochloroacetic acid and glycollic acid as well as the anions derived from these species account for anoticeable percentage of iodine disappearance through a side reaction, it would seem that a natural course of action would be the study of the kinetics of the tautomeric shift in these species. Experimental evidence obtained in the present work shows

° R. Bell and E. Caldin, J. Chem. Soc., 382, (1938)

that as the concentrations of certain acids and anions are increased, iodine disappears more rapidly, despite the fact that there is no acetone present. Careful observations should reveal certain quantitative relationships.

In addition, it would be of some value to calculate the isotope effect involved in the k_T term of the polymolecular scheme, $k_T[ACID][ANION]$. Values for the concentrations such as tje ones used in this work could not be expected to show a detectable product.

Finally, the comparison of techniques (titration, spectrophotometry, potentiometry and polarography) as to speed, accuracy and flexibility under varying conditions would provide perhaps the best basis for more advanced study.

TABLE III

LIST OF SLOPES FOR THE DISAPPEARANCE OF I_2

Acetic acid / Acetate		Trimethylacetic acid / Trimethylacetate	
SLOPES			SLOPES
R = 1.0			R = 1.0
.150 M Anion	438, 444, 449 *	.150	667, 695
.112	324, 326	.112	521, 528
.090	242, 258	.090	395, 372
.070	183, 188	.060	236, 217, 215
R = 3.5×10^{-1}		R = 5.0×10^{-1}	
.150	389, 400, 411	.125	513, 508
.112	311, 297, 312	.100	396, 381
.090	232, 211, 21o, 216	.075	290, 287
.070	197, 210, 189, 203	.045	166, 17o

* i.e. 4.49×10^{-5} O.D.U./min.

TABLE III

LIST OF SLOPES FOR THE DISAPPEARANCE OF I_2

Monochloroacetic acid / Monochloroacetate		Glycollic acid / Glycollate	
	SLOPES		SLOPES
	$R = 2.6 \times 10^{-2}$		$R = 1.0 \times 10^{-1}$
.150 M Anion	315, 292, 310, 427, 313 *		158, 119, 123, 111, 117
.112	211, 219, 218, 232		866, 811, 867
.090	216, 192		588, 739, 746, 507, 572
.070	155, 157		480, 474, 489, 432
	$R = 1.6 \times 10^{-2}$		$R = 3.0 \times 10^{-1}$
.150	277, 214, 208, 211		117, 108
.112	217, 215, 197		986, 1000, 966
.090	265, 167,		452, 506, 654, 776
.070	133, 130, 138, 132		497, 498

* i.e. 3.13×10^{-4} $\Delta OD/hr.$

ADDENDA

TABLE III

Slopes for the disappearance of iodine catalyzed by H_3O^+

LIGHT ACETONE	HEAVY ACETONE
1.19×10^{-5} O.D.U./sec.	2.15×10^{-6}
1.37×10^{-5} O.D.U./sec. (.150M NaCl)	2.16×10^{-6}
1.28×10^{-5} O.D.U./sec. (.150M KI)	

TABLE IV

Calculated slopes corresponding to B and D in figure 7, p. 29

ACID	R	SLOPES
Monochloroacetic acid	2.6×10^{-2}	6.5×10^{-7} (in hours)
	1.6×10^{-2}	5.89×10^{-7}
Glycollic acid	1.0×10^{-1}	2.92×10^{-6}
	3.0×10^{-1}	3.55×10^{-6}
Trimethylacetic acid	1.0	8.84×10^{-6} (in minutes)
	5.0×10^{-1}	8.24×10^{-6}
Acetic acid	1.0	
	3.5×10^{-1}	5.2×10^{-6}

ADDENDA

General Method of Calculation:

The individual values for the catalysis (slopes as listed in Table III) are plotted vs. concentration of anion. The slope of this new plot is adjusted to give the results in the reported units. This slope is now set equal to the term containing R, k_A and k_B; the other slope (corresponding to R′)is treated in axactly the same way, leaving two unknowns and two equations with which to solve them.

Sample Calculation:

The method outlined above will be illustrated using the experimental results obtained for the reaction catalyzed by acetic acid and acetate ions.

Plotting each value for optical density-- time vs. the concentration of anion using buffer ratio R leads to a curve with slope equal to $\frac{1}{3.08 \times 10^{3}} \frac{\text{ODU}}{\text{mole acetate/min.}}$

Utilizing the relation that each ODU corresponds to 1.39×10^{-3} moles I_2 /liter, one may write:

$$1.39 \times 10^{-3} \frac{\text{moles } I_2 \text{/liter}}{\text{ODU}} \times \frac{1}{3.08 \times 10^{3}} \frac{\text{ODU}}{\text{mol acetate/min}}$$

or $4.52 \times 10^{-7} \frac{\text{moles } I_2 \text{/liter}}{\text{mole acetate/minute}}$. This figure corresponds to an iodine concentration of 7.09×10^{-2} moles/liter. Adjusting the above expression to give the disappearance referred to one mole/liter of acetone(Heavy):

$$4.52 \times 10^{-7} \frac{\text{moles } I_2 \text{/liter}}{\text{moles acetate/min}} \div 7.09 \times 10^{-2} \frac{\text{moles acetone}}{\text{liter}}$$

ADDENDA

giving a final expression of

6.370×10^{-6} moles I_2 /liter per mole acetate per minute, for the disappearance of iodine. Setting this equal to the term involving the specific rate constants results in $\frac{6.370 \times 10^{-6} \text{ moles } I_2 \text{/liter}}{\text{mole acetate/minute}} = k_B + k_A R$, where R = 1. Following the same procedure for the other R value results in the second of the two equations, allowing solution for the two unknowns.

Since the plot of rates vs. anion concentr ations contained only four points, the curve was drawn by a visual method, so that the error inherent in the four points would not have a very large effect on the slope as a whole. In other words, all the runs corresponding to each of the four points wereplotted, rather than averaging them and calculating the least squares plot. This method led to a reprcduction of slopes to within a few percent.

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